

# REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-018 4302). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to provide information unless it is specifically required by law. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

0273

1. REPORT DATE (DD-MM-YYYY) 07/10/2003		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 02/01/02 - 12/31/02	
4. TITLE AND SUBTITLE "Absolute Cross Sections for Collision-Induced Dissociation Reactions of Highly Vibratioinnally Excited ... Ions"				5a. CONTRACT NUMBER F49620-02-1-0120	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Dr. Cheuk-Yiu Ng				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, Davis Chemistry Department One Shields Avenue Davis, CA 95616				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Air Force AFOSR 4015 Wilson Blvd, Rm 713 Arlington, VA 22203-1954				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES NONE					
14. ABSTRACT See attached summary of results					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Cheuk-Yiu Ng
a. REPORT Unclassified	b. ABSTRACT	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (530) 754-9645

20030731 061

# Final Report on "Absolute Cross Sections for Collision-Induced Dissociation Reactions of Highly Vibrationally Excited $O_2^+(X^2\Pi_{3/2,1/2g}$ and $a^4\Pi_{5/2,3/2,1/2,-1/2u})$ Ions "

Cheuk-Yiu Ng<sup>a)</sup> and Rainer A. Dressler<sup>b)</sup>

*a) Department of Chemistry, University of California at Davis, Davis, CA 95616*

*b) Air Force Research Laboratory, Hanscom AFB, MA 01731*

## I. Summary of results

During the past funding cycle, we have constructed and successfully integrated a state-of-the-art guided-ion beam mass spectrometer into the high-resolution photoion-photoelectron apparatus (Endstation 2) of the Chemical Dynamics Beamline at the Advanced Light Source (ALS) for the study of ion-molecule reaction dynamics. Preliminary tests on the performance of this guided-ion beam mass spectrometer have been made, indicating that the apparatus is performing well. Using this apparatus, we have measured the collision-induced dissociation (CID) and charge transfer (CT) cross sections for the collisions of  $O_2^+(v^+=0-3) + Ar$ .

Most importantly, by employing the differential pulse ion gate scheme along with the novel application of a wired ion gate to reject false coincidence ions, we have demonstrated for the first time a sensitive pulsed field ionization-photoelectron (PFI-PE)-secondary ion coincidence (PFI-PESICO) method for absolute cross section measurements of state-selected ion-molecule reactions. The high-resolution achieved by this PFI-PESICO method allows the unambiguous internal state selection of simple ions not only in specific vibronic levels, but also in given rotational states.

## II. Results of test experiments

### A. $ArD^+$ from $Ar^+(^2P_{3/2,1/2}) + D_2$

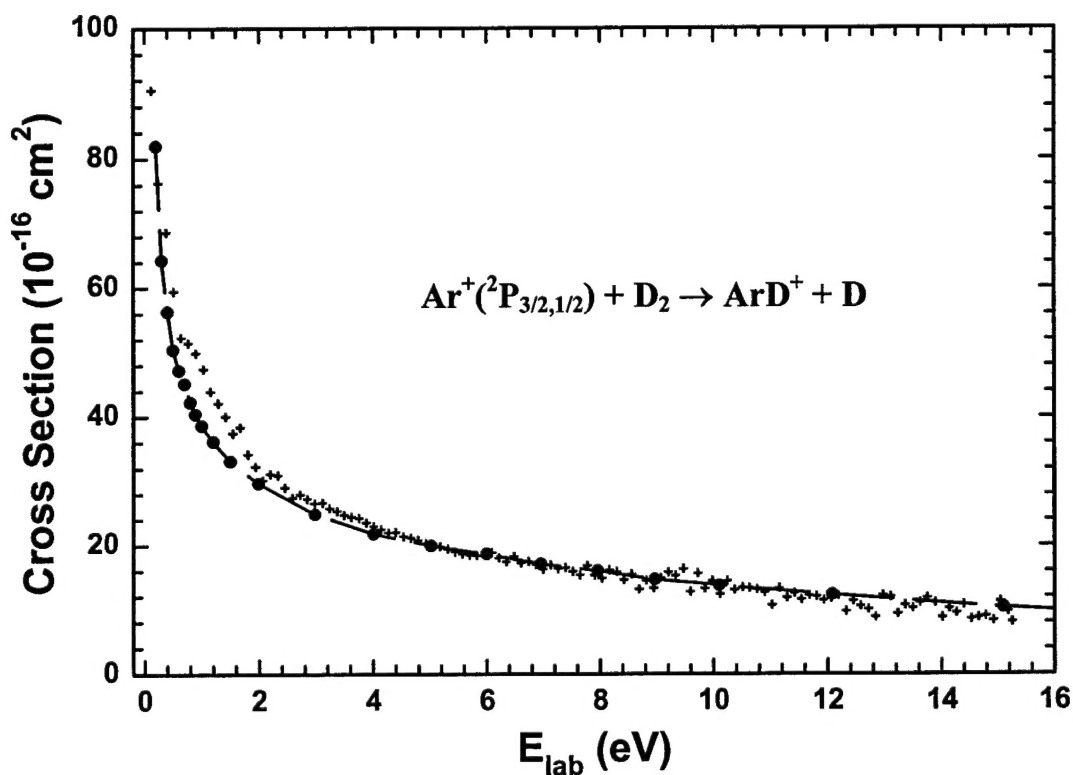
Absolute total cross sections for reaction (1) have been accurately measured by Ervin and Armentrout [*J. Chem. Phys.* **83**, 166 (1985)] over a wide collision energy range. These cross-sections for the formation of  $ArD^+(\bullet)$  in the laboratory kinetic energy ( $E_{lab}$ ) range of 0.2-10 eV are

**DISTRIBUTION STATEMENT A**  
Approved for Public Release  
Distribution Unlimited

compared in Fig. 1 to those (+) measured in the  $E_{\text{lab}}$  range of 0.02-10 eV using the newly constructed ion-molecule reaction photoionization apparatus at the ALS.

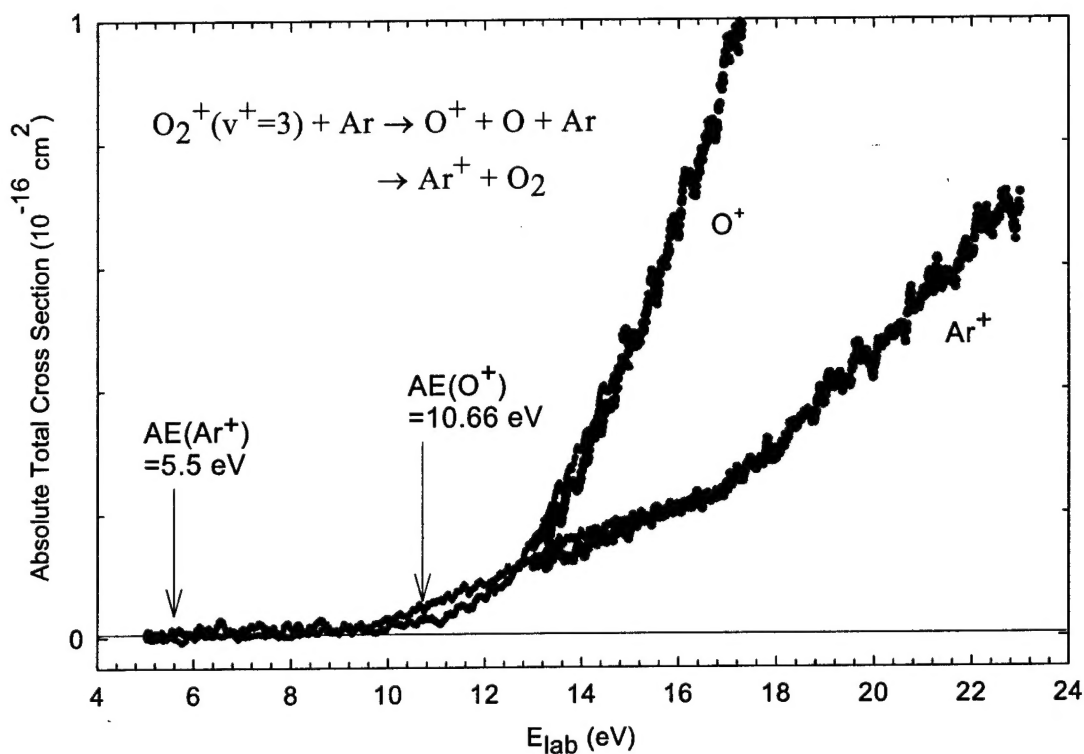


As shown in Fig. 1, the general agreement between the two experiments are good after taking into account uncertainties of both experiments. The reactant  $\text{Ar}^+(\text{}^2\text{P}_{3/2,1/2})$  ions are prepared by electron-impact ionization in the experiment of Ervin and Armentrout, while those in the ALS experiment are formed by photoionization. The good agreement observed in this test experiment indicates that the kinetic energy resolution achieved using the ion-molecule reaction photoionization apparatus is sufficiently narrow and is capable of providing reliable reaction cross sections down to thermal collision energies.



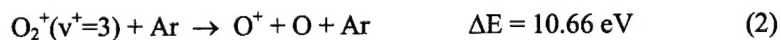
**Figure 1.** Absolute total cross sections for reaction (1). The data points in solid dots are reported by Ervin and Armentrout, whereas those in crosses are obtained using the ion-molecule reaction photoionization apparatus at the ALS.

$\text{O}^+$  from  $\text{O}_2^+(\text{X}^2\Pi_g, v^+=3) + \text{Ar}$



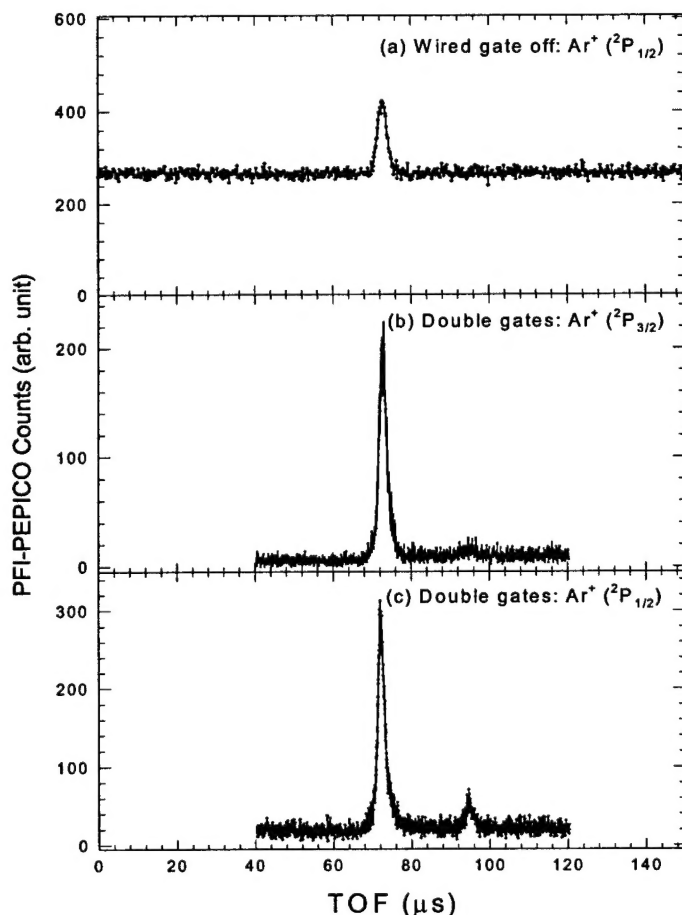
**Figure 2.** Absolute total cross sections for the formation of  $\text{O}^+$  and  $\text{Ar}^+$  from  $\text{O}_2^+(v^+=3) + \text{Ar}$  in the  $E_{\text{lab}}$  range of 5-23 eV.

In a recent experiment, we have measured the CID and CT cross sections for the reaction of  $\text{O}_2^+ + \text{Ar}$  (Ne) [Dressler et al., J. Chem. Phys. **113**, 8561 (2000)]. In the latter experiment, reactant  $\text{O}_2^+$  ions are prepared by ionization of  $\text{O}_2$  using an electron beam at  $13.0 \pm 0.5$  eV. Thus,  $\text{O}_2^+$  can be formed in a distribution of vibrational states with  $v^+$  up to 6. Figure 2 shows the absolute total cross sections for  $\text{O}^+$  and  $\text{Ar}^+$  formed by reactions (2) and (3), respectively, obtained using the ion-molecule reaction photoionization apparatus.



In this experiment, reactant  $\text{O}_2^+$  ions are predominantly formed in the  $v^+=3$  state using the nearby resonance autoionizing Rydberg level just above the IE for the formation of  $\text{O}_2^+(v^+=3)$ . As expected, although these cross section curves are similar to those reported recently by Dressler et al., the absolute cross sections are different. The thresholds or appearance energies (AEs) observed for  $\text{O}^+$  and  $\text{Ar}^+$  (marked in Fig. 2) are in excellent agreement with the thermochemical thresholds of 10.66 eV and 5.5 eV for reactions (2) and (3), respectively. The step observed for the  $\text{Ar}^+$  cross-section curve in the  $E_{\text{lab}}$  range of 12-18 eV is indicative of the opening of the CID channel. This experiment demonstrates that reaction cross sections down to the  $10^{-19} \text{ cm}^2$  can be measured using the ion-molecule reaction photoionization apparatus at the ALS.

### III. PFI-PESICO MEASUREMENTS



**Figure 3.** PFI-PESICO bands for  $\text{Ar}^+ (^2P_{1/2})$  obtained (a) without using the wired gate and (c) using the wired gate. (c) is the PFI-PESICO band for  $\text{Ar}^+ (^2P_{3/2})$  obtained using the wired gate.

The goal of this experimental project is to perform PFI-PESICO measurements on state-selected diatomic ions. Instead of detecting the correlated PFI-PEs and PFI-PIs formed in the PFI process, we would look for correlated PFI-PEs and secondary ions formed by the reaction of PFI-PIs. The PFI-PESICO experiments are significantly more difficult than PFI-PEPICO experiments [Jarvis et al., *Rev. Sci. Instrum.* **70**, 3892 (1999)] because the intensities for reaction product ions resulting from collisions between the PFI-PIs and neutral reactants are usually less than 1% that of the PFI-PIs.

Furthermore, the product ions are most likely scattered and dispersed in time, arriving at the ion detector with a significantly broader temporal distribution. Thus, the false coincidence background is expected to be much higher than that observed in PFI-PEPICO measurements for unimolecular dissociation studies. The ion-molecule photoionization apparatus employs two octopole ion-guides for confining reactant and product ions and a QMS for mass detection of reactant and product ions. It is well known that the rf-field is a non-conservative field and thus rf-devices, such as the QMS and octopoles, have the effect of broadening the ion TOF peaks. The PFI-PEPICO TOF peak for  $\text{Ar}^+$  observed previously using a linear TOF mass spectrometer was found to have a FWHM of  $\approx 300$  ns. This compares to FWHMs of 3-6  $\mu\text{s}$  for the  $\text{Ar}^+(^2\text{P}_{3/2})$  PFI-PEPICO TOF peaks [see Figs. 3(a) and 3(b)] observed using the ion-molecule reaction photoionization apparatus. Consequently the false coincidence background for the PFI-PEPICO band for  $\text{Ar}^+(^2\text{P}_{1/2})$  found in Fig. 3(a) is expected to be 10-20 times higher than that observed using the linear TOF mass spectrometer. We note that the PFI-PEPICO peak for  $\text{Ar}^+(^2\text{P}_{1/2})$  depicted in Fig. 3(a) was obtained using procedures similar to those reported previously. The false coincidence background of the spectrum shown in Fig. 3(a) has the same intensity as that for the coincidence  $\text{Ar}^+$  peak. This high false coincidence background may prevent successful PFI-PESICO measurements. We have overcome this difficulty by using a novel wired gate lens [Brock et al., *Rev. Sci. Instrum.* **71**, 1306 (2000)] to eliminate most of the false coincidence ions. Using this lens, no ions are allowed to transmit to the ion detector unless a PFI-PE is detected at the electron MCP detector, which signifies the creation of a "true" coincidence ion. The wired gate lens is basically a grid lens constructed by parallel wires with a separation of 0.0125" between adjacent wires. By applying alternative positive and negative potentials of identical magnitudes to these wires, ions are

effectively deflected away from the beam path as they pass through the grid. Because of the small distance between adjacent wires, a small potential difference of a few volts applied to adjacent wires is sufficient for deflecting the false ions. This deflecting field should not affect the trajectories of ions at a finite distance from the wired gate lens because the alternate positive and negative potentials seen by these ions are essentially canceled. As shown in Figs. 3(b) and 3(c), the PFI-PEPICO TOF peaks for  $\text{Ar}^+(^2\text{P}_{3/2})$  and  $\text{Ar}^+(^2\text{P}_{1/2})$  obtained using the wired gate lens have nearly zero false coincidence background. This is a very encouraging result. After fine-tuning the operation conditions of the wired gate lens, we have demonstrated the PFI-PESICO method for rovibrational-state-selected studies of the ion-molecule reactions  $\text{H}_2^+(\nu^+=0-18 \text{ } N^+=1) + \text{Ar (Ne)}$  using the ion-molecule reaction photoionization apparatus.

#### IV. Refereed journal publications (2001-2003)

The support of AFOSR has been acknowledged in the following articles.

- Y. Song, C. Y. Ng, G. Jarvis, and R. Dressler, "Rotational-Resolved Pulsed Field Ionization-Photoelectron Study of  $\text{NO}^+(\text{A}^1\Sigma^-, \nu^+ = 0-17)$  in the Energy Range of 17.79-20.10 eV", *J. Chem. Phys.* **115**, 2101-2108 (2001).
- K.-M. Weitzel, G. Jarvis, M. Malow, Y. T. Baer, Song, and C. Y. Ng, "Observation of Accurate Ion Dissociation Thresholds in Pulsed Field Ionization Photoelectron Studies", *Phys. Rev. Lett.* **86**, 3526 (2001).
- J. Liu, M. Hochlaf, G. Chambaud, P. Rosmus, and C. Y. Ng, "High Resolution Pulsed Field Ionization-Photoelectron Bands for  $\text{CS}_2^+(\text{A}^2\Pi_u)$ : An Experimental and Theoretical Study", *J. Phys. Chem.* **105**, 2183 (2001).
- D. G. Fedorov, M. S. Gordon, Y. Song, and C. Y. Ng, "A Theoretical Study of the Spin-orbit coupling in  $\text{O}_2^+(\text{A}^2\Pi_{3/2,1/2u}, \nu^+=0-15; \text{a}^4\Pi_{5/2,3/2,1/2,-1/2u}, \nu^+=0-18)$ ", *J. Chem. Phys.* **115**, 7393 (2001).
- X.-M. Qian, Y. Song, K.-C. Lau, C. Y. Ng, J. Liu, W. Chen, and G.-Z. He, "A Pulsed Field Ionization Study of the Reaction  $\text{D}_2\text{O} + h\nu \rightarrow \text{OD}^+ + \text{D} + \text{e}^-$ ", *Chem. Phys. Lett.* **353**, 19-26 (2002).
- C. Y. Ng, "Vacuum Ultraviolet Spectroscopy and Chemistry Using Photoionization and Photoelectron Methods", *Ann. Rev. Phys. Chem.* **53**, 101-140 (2002).

- Wenwu Chen, M. Hochlaf, P. Rosmus, G.-Z. He, and C. Y. Ng, "Vacuum Ultraviolet Pulsed Field Ionization Photoelectron Study of OCS in the Energy range of 15.0-19.0 eV", *J. Chem. Phys.* **116**, 5612 (2002).
- C. Y. Ng, "State-Selected and State-to-State Ion-Molecule Reaction Dynamics", *J. Phys. Chem. (Feature Article)*, **A106**, 5952-5966 (2002).
- Y.-J. Chen, P. T. Fenn, K.-C. Lau, C. Y. Ng, C.-K. Law, and W.-K. Li, "A Study of the Dissociation of  $\text{CH}_3\text{SCH}_3^+$  by Collisional Activation: Evidence of Non-Statistical Behavior", *J. Phys. Chem.* **A106**, 9729 (2002).
- Jianbo Liu, Wenwu Chen, M. Hochlaf, Ximei Qian, Chao Chang, and C. Y. Ng, "Unimolecular Decay Pathways of State-Selected  $\text{CO}_2^+$  in the Internal Energy Range of 5.2-6.2 eV: An Experimental and Theoretical Study", *J. Chem. Phys.* **118**, 149 (2003).
- X. M. Qian, T. Zhang, Y. Chiu, D. J. Levandier, J. S. Miller, R. A. Dressler, and C. Y. Ng, "Rovibrational State-Selected Study of  $\text{H}_2^+(X, v^+=0-17, N^+=1)+\text{Ar}$  Using the Pulsed Field Ionization-Photoelectron-Secondary Ion Coincidence Scheme", *J. Chem. Phys. (communication)*, **118**, 2455 (2003).
- Jianbo Liu, M. Hochlaf, and C. Y. Ng, "Pulsed Field Ionization-Photoelectron Bands for  $\text{CS}_2^+$  in the Energy Range of 13.2 - 17.6 eV: An Experimental and Theoretical Study", *J. Chem. Phys.* **118**, 4487 (2003).
- Ximei Qian, Andy Kung, Tao Zhang, and Cheuk-Yiu Ng, "Two-Color Photoionization Spectroscopy Using Vacuum Ultraviolet Synchrotron Radiation and Infrared Optical Parametric Oscillator Laser Source", *Rev. Sci. Instrum.* **74**, 2784-2790 (2003).
- Wenwu Chen, Jianbo Liu, and C. Y. Ng, "Vacuum Ultraviolet Pulsed Field Ionization-Photoelectron Study for  $\text{N}_2\text{O}^+$  in the Energy Range of 16.3 - 21.0 eV", *J. Phys. Chem. A*, web-published April 11, (2003).
- X.-M. Qian, T. Zhang, C. Chang, P. Wang, C. Y. Ng, Y.-H. Chiu, D. J. Levandier, J. S. Miller, R. A. Dressler, T. Baer, and D. S. Peterka, "High-Resolution State-Selected Ion-Molecule Reaction Studies Using Pulsed Field Ionization Photoelectron-Secondary Ion Coincidence Method", *Rev. Sci. Instrum.*, accepted.